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(54) FAT EMULSIONS

(71) We, UNILEVER LIMITED, a company registered under the laws of Great Britain, of Port Sunlight, Birkenhead, Cheshire, England, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to fat emulsions and to processes for their preparation.

Although modern developments, for instance the use of scraped surface tubular heat exchangers, have enabled the production of margarine of good quality having many butter-like properties, improvement of the consistency behaviour of margarine remains the subject of research. This invention is concerned with the production of fat emulsions, especially margarine, having an improved consistency behaviour.

In the manufacture of butter, milk with a fat content of about 3.5% is centrifuged and a cream fraction of higher fat content, for example from 35 to 80%, obtained. This fraction is an oil-in-water emulsion. It is bacterially soured if required, cooled and mechanically worked, for example in a butter machine; this working effects phase-inversion with the formation of the characteristic water-in-oil emulsion structure of butter. Using cream of about 35 to 50% fat content, during phase-inversion a part of the aqueous phase separates as buttermilk, while using cream of about 80% fat content there is no separation of aqueous phase.

Butter has a microscopic form that is clearly differentiatable from normal margarine and is characterised by a non-uniform division of water droplets, very fine crystallisation, and the presence of so-called "fat globules". The presence of fat globules and this kind of water division is associated with the characteristic plasticity and elasticity of butter that distinguishes it from normal margarine. The phase-inversion step in butter manufacture evidently plays an important part in achieving the characteristic structure of butter. Reduction of the plasticity and elasticity of butter is observed when it is intensively worked, for example by homogenisation, and the number of fat globules is simultaneously reduced and the fine division of the aqueous phase is increased.

Margarine is an emulsion of edible fat and, like butter, a water-in-oil emulsion. In modern margarine processes a water-in-oil emulsion is prepared, for example, by passing the aqueous and the oil phases simultaneously through emulsifying machines. It is also possible to prepare an oil-in-water emulsion first, and to produce a margarine from it by cooling and mechanically working it so that phase-inversion occurs as in butter manufacture, but in practice it has been found that oil-in-water emulsions that are stable are difficult to prepare, especially those with a fat content as high as that in the finished margarine, and which are converted to margarine by phase-inversion without separation of an aqueous phase. For emulsions of this kind special emulsifying equipment has hitherto been necessary in order to divide the fat droplets in the aqueous phase sufficiently. Moreover such emulsions have hitherto had the disadvantage of poor stability in making phase-inverted emulsions at a pH in the acid range,

for example, between 4 and 5, and such a pH is desirable for keepability of margarine.

The present invention is concerned with stable oil-in-water emulsions prepared using a special emulsifier which confers properties enabling phase-inversion margarines with butter-like elasticity and plasticity to be obtained. The emulsifier concerned is a monoacylglycerophosphatide.

The emulsions of this invention are aqueous fat emulsions containing phosphatide at least 15% by weight of which is a monoacylglycerophosphatide whose acyl group is derived from a fatty acid having at least 8 carbon atoms in the molecule.

Such emulsions include both oil-in-water emulsions and the water-in-oil emulsions obtained from them by phase inversion. By "fat" is meant a fatty acid triglyceride in either the liquid or solid state, and by "oil-in-water" and "water-in-oil" is meant the type of emulsion irrespective of the state of the fat. Preferably the fat is an edible fat.

The fat used can be a vegetable fat, for instance coconut oil or a margarine oil blend, or butter oil. It can contain a small amount of fatty acid monoglyceride, for instance from 0.05 to 0.5%. In practice the emulsion will contain from 3 to 85%, and preferably from 60 to 85%, of fat by weight.

Monoacylglycerophosphatides lack one of either the α- or β-acyl groups of diacylglycerophosphatides, and typical of them are α- and β-lysolecithin and α- and β-lysocephalin. Monoacylglycerophosphatides can be prepared by synthesis or they can be obtained by the chemical or enzymatic partial hydrolysis of diacylglycerophosphatides. α-Monoacylglycerophosphatides can be prepared by the action on diacylglycerophosphatides of the enzyme phospholipase A (lecithinase A), which is conveniently prepared free of other enzymes by the partial heat-inactivation of pancreatin. For this an aqueous suspension of pancreatin can be heated to from 70° to 80°C for 30 minutes or to 90°C for 10 minutes. The phosphatide used for the hydrolysis can be a phosphatide slime obtained in the production of plant oils, for example soyabean oil or rapeseed oil, and steam or water treatment of the extracted oils at 95° to 100°C, or the crude phosphatide obtained by centrifuging such a phosphatide slime and drying the product under reduced pressure: a typical crude phosphatide thus obtained contains about 65% diacylglycerophosphatides and 35% oil. Alcohol-insoluble and alcohol-soluble fractions of these crude phosphatides can be used, especially alcohol-soluble ones with a proportion by weight of phosphatidylcholine (lecithin) to phosphatidylethanolamine (cephalin) of at least 4 to 1, such as those described in British Patent 1,113,241. Egg yolk phosphatides and specific diacylglycerophosphatides, for example cephalin and lecithin can also be used.

In preparing an α-monoacylglycerophosphatide by enzymic hydrolysis of such a phosphatide the latter is dissolved or suspended in water, or a solvent containing sufficient water, with from 0.1 to 25% of heat-treated pancreatin by weight of the phosphatide, and hydrolysis allowed to proceed at ambient temperature until a sufficient concentration of the monoacyl compound has been formed. Preferably the water contains calcium ions and tap water of 5 to 30° hardness is suitable. Fatty acid produced and contaminating fat can subsequently be removed by drying the product, for instance by evaporation under reduced pressure, and extracting it with acetone. A phosphatide containing from 15 to 70% of monoacylglycerophosphatide, depending on the degree of hydrolysis effected, can be obtained in this way. The amount of monoacylglycerophosphatide in the product of hydrolysis can be determined by standard analytical methods, for instance thin layer chromatography.

In practice the fatty acid acyl group of the monoacylglycerophosphatide has at least 10 carbon atoms, and the monoacylglycerophosphatide produced from a natural phosphatide will generally have its monoacyl group derived from mixed fatty acids, especially those of 16 and 18 carbon atoms. Preferably at least 20% and especially at least 25% of the phosphatide used is monoacylglycerophosphatide. Preferably also the monoacylglycerophosphatide comprises lysolecithin and lysocephalin, the proportion of lysolecithin to lysocephalin being at least 4 to 1 by weight.

In preparing the fat emulsions sufficient of the monoacylglycerophosphatide is used to obtain the stability required: the amount used is generally within the range of from 0.1 to 15% by weight of the fat, and normally in preparing margarine emulsions from 0.1 to 2% is suitable.

Preferably the emulsion also contains a water-soluble protein, as this assists in its stabilisation, particularly when the emulsion contains more than 40% by weight of fat, and preferably at least 0.1%, especially more than 0.25%, of such protein by weight of the fat is present. Milk protein, for instance as casein, whey or skim milk, or a suitable soya protein can be used.

In a process of the invention a fat emulsion is prepared by emulsifying liquid fat with an aqueous dispersion of the monoacylglycerophosphatide - containing phosphatide to produce an oil-in-water emulsion. The aqueous dispersion can be made by mixing the phosphatide containing mono-

acylglycerophosphatide with the remainder of the aqueous phase, for instance skim milk, and heating if necessary: the fat can then be stirred into the aqueous dispersion at a temperature at which the fat is liquid. Care should be taken to regulate the addition of the fat so that a local excess is avoided in order to ensure production of an oil-in-water emulsion: this is particularly important where the fat content of the emulsion required is above 70%.

As the emulsifying properties of monoacylglycerophosphatides are not affected by alkaline earth metal ions it is possible to use hard water or calcium-containing protein solutions without the addition of complex-forming salts or acids. Moreover the aqueous phase can contain up to 5% of salt.

The pH of the aqueous phase can be from 2 to 7, as the monoacylglycerophosphatides have been found to have a stabilising action on proteins so that they are not precipitated at the isoelectric point. This gives a special advantage in that the aqueous phase can be made acid in the presence of protein before the emulsification of the fat phase, if this is desired, rather than making the final emulsion acid. For margarine an acid pH is preferable on bacteriological grounds. The aqueous phase or the formed emulsion can be made acid to the required pH with lactic, citric, or other suitable acid, or by the action of bacteria, for instance with addition of 0.5 to 1% of lactic acid culture where the appropriate bacterial substrate is present. Preferably the pH of the emulsion is from 4 to 5.

The oil-in-water emulsions obtained can if required be homogenised at elevated temperature, for instance at 40 to 70°C, and can be pasteurised or sterilised.

Milk-like emulsions with a fat content of 3 to 15% thus prepared can be concentrated by centrifugation to higher fat contents, for example to a fat content of about 35 to 85% for further working to margarine. The separated aqueous phase can be used again for the preparation of further emulsion.

The oil-in-water fat emulsions of 35 to 85% fat content can be converted to water-in-oil emulsions with a butter-like structure by cooling and working to cause phase inversion.

An oil-in-water emulsion of 35 to 60% fat content can be cooled to about 5 to 15°C to crystallise at least part of the fat and then worked by stirring or kneading to effect phase inversion. The structural changes observed during working correspond to the buttering-out process using medium-fat cream. The inversion process is complete in a few minutes when part of the aqueous phase separates, corresponding to buttermilk separation in making butter. The water content of the product is between 12 and 18%, and this can be further adjusted if required by kneading, if necessary with added water or sour milk; such further working can also reduce the proportion of "free water", and thus increase stability of the product.

Protein-containing oil-in-water emulsions of particularly high fat content, for example 80%, can also be converted directly by phase-inversion into margarine. The direct preparation of such high fat protein-containing oil-in-water emulsions has hitherto been very difficult because of the danger of a sudden breakdown of structure of the uncrystallised oil-in-water emulsions. This difficulty arises because when the fat content of the emulsion is increased from 70 to 80%, about 40% of the total fat contained in the 80% emulsion still remains to be introduced into the 70% emulsion.

The monoacylglycerophosphatides used as emulsifiers in the emulsions of this invention enable the preparation of these emulsions of such high fat content. A higher protein content than is provided by the use of skim milk can be achieved by the use of milk powder.

The high fat oil-in-water emulsions are cooled, for instance to 8—10°C and partially crystallised before the phase-inversion. By the adoption of a suitable procedure, for example rapid cooling without strong mechanical working, as in a cooling drum, or by slow cooling without disturbance, the onset of premature phase-inversion can be prevented. The cooled emulsion can then be phase-inverted, preferably by stirring or kneading. The margarine obtained by this inversion process shows the desired consistency characteristics of a similarly prepared butter: it possesses high plasticity and elasticity, is pleasantly fresh in taste and shows "fat globules" of microscopic form typical of those for butter.

A margarine showing butter-like consistency can also be produced by partial phase-inversion. Thus 4 parts of a cooled 74% oil-in-water emulsion can be mixed with one part of the likewise cooled uncrystallised fat composition so that at the same time phase-inversion of the oil-in-water emulsion occurs.

The cooling temperatures in the phase inversion process can be in the range of from 5 to 15°C, and should in any case be at least 5°C below the melting point of the fat phase.

The invention is illustrated by the following Examples, in which all temperatures are in °C.

EXAMPLE 1

A crude soya phosphatide (100 g) containing 65% diacylglycerophosphatide and 35% oil was suspended in tap water (200

cc) of 17° hardness, and to this suspension was added pancreatin (1 g) that had previously been heated to 75° for 30 minutes: the mixture was stirred for 5½ hours at 22° and then dried by evaporation at 40° under reduced pressure. The resulting partially hydrolysed phosphatide was water-dispersible and had an acid number of 41; fat and free fatty acid were then removed by acetone extraction and analysis showed the product had a content of 15% α-monoacylglycerophosphatides by weight.

To a mixture of tap water (100 g) and skim milk (100 g) was added the partially hydrolysed phosphatide (2 g, containing about 0.3 g monoacylglycerophosphatide) and after it had been dispersed groundnut oil (200 g) was added and the mixture emulsified at 60°. The 50% oil-in-water emulsion obtained was allowed to stand at 60° for 20 hours, after which only 2% of the aqueous phase had separated, and the viscosity of the emulsion at a shear rate $D=10\ sec^{-1}$, measured using a Ferranti rotation viscometer ("Ferranti" is a Registered Trade Mark), was 38 cP.

EXAMPLE 2

A phosphatide fraction obtained by the extraction of crude soya phosphatide with alcohol contained a proportion of lecithin to cephalin by weight of 4 to 1. A 35% solution of it by weight in refined soya oil was dispersed in twice its weight of tap water and to the suspension was added 2% of the heat-treated pancreatin of Example 1 by weight of the phosphatide fraction and the mixture maintained at 22° for 6 hours and afterwards dried by evaporation under reduced pressure at 40°. The dried product was added to ten times its volume of acetone with stirring at 0°, the mixture filtered and solvent removed from the residue at below 50° under reduced pressure. A partially hydrolysed phosphatide free of fat and fatty acid with an α-monoacylglycerophosphatide content of 35% by weight was obtained.

A 50% oil-in-water emulsion was prepared as in Example 1 using 0.25% by weight of the partially hydrolysed phosphatide (0.17% of monoacylglycerophosphatide by weight of the fat) and allowed to stand at 60° for 20 hours, after which it showed a water separation of only 1% and a viscosity of 10 cP.

EXAMPLE 3

A crude soya phosphatide (100 g) was dispersed in twice its weight of water, the heat-treated pancreatin of Example 1 (25 g) was added and the mixture twice extracted with ether (1 litre). The water-saturated ether extract was allowed to stand at 22° for 3½ hours and the ether was then distilled off and the phosphatide residue dried under reduced pressure at 40°. The water-dispersible partially hydrolysed phosphatide thus obtained was lighter in colour than the starting crude phosphatide, and after removal of fat and free fatty acid by acetone extraction was found to contain 20% by weight of monoacylglycerophosphatides.

A 50% oil-in-water emulsion was prepared as in Example 1 using 2% of the partially hydrolysed phosphatide by weight (0.8% of monoacylglycerophosphatide by weight of the fat): after allowing it to stand for 20 hours at 60° no water separation had occurred: and the emulsion then had a viscosity of 10 cP.

EXAMPLE 4

The alcohol-soluble soya phosphatide fraction of Example 2 was hydrolysed using the conditions of Example 3 except that the reaction time was 8 hours. The ether-insoluble monoacylglycerophosphatide product precipitated out together with unchanged phosphatides, while the fatty acids formed by the reaction remained dissolved. The supernatant ether solution was decanted and the residue dried under reduced pressure at 40° to give a water-soluble partially hydrolysed phosphatide containing 45% by weight of monoacylglycerophosphatides.

A 50% oil-in-water emulsion was prepared as in Example 1 using 0.25% by weight of the partially hydrolysed phosphatide (0.2% of monoacylglycerophosphatide by weight of the fat) and allowed to stand at 60° for 20 hours, after which it showed no water separation and a viscosity of 15 cP.

EXAMPLE 5

To sour skim milk (100 g) was added the partially hydrolysed phosphatide of Example 4 (2.5 g) and after it had been dispersed groundnut oil (400 g) was added and the mixture emulsified at 60°. The 80% oil-in-water emulsion obtained (containing 0.28% of monoacylglycerophosphatide by weight of the fat) was pourable, and after 20 hours at 60° showed no water or oil separation and a viscosity of 39 cP; it remained stable after further acidification with citric acid to pH 4.0.

EXAMPLE 6

A partially hydrolysed defatted soya phosphatide (6 parts by weight) containing 25% lysolecithin and 20% lysocephalin by weight, which had been prepared from a crude soya phosphatide by enzymatic hydrolysis with phospholipase A, was dispersed in a mixture of skim milk (200 parts) and water (200 parts), the dispersion heated to 65° and a margarine fat blend (600 parts) at 70° added while the mixture was vigorously stirred using a turbine stirrer. The resulting 60% oil-in-water emulsion was homogenised at

70° and then showed a uniform fat droplet size with a mean droplet diameter of 3μ. 90% Aqueous lactic acid solution was added until the pH of the emulsion was 4.5, and the acidified emulsion was then coled to 8°. The partially crystallised oil-in-water emulsion thus obtained was then phase-inverted at 8 to 12° by agitation in a Hobart mixer ("Hobart" is a Registered Trade Mark) for 8 minutes. The aqueous phase which separated (265 parts) was removed, leaving a phase-inverted margarine (720 parts). The product was kneaded for a short time to give a margarine containing 82% fat which was butter-like in its plasticity, elasticity, taste impression and form seen under the microscope.

EXAMPLE 7

A partially hydrolysed defatted soya phosphatide fraction (8 parts by weight) containing 33% lysolecithin and 8% lysocephalin by weight, which had been obtained by enzymatic hydrolysis of an alcohol-soluble soya phosphatide fraction having a relative proportion of lecithin to cephalin of 4.9 to 1, was dispersed at 75° in skim milk (200 parts), which had previously been brought to pH 4.5 by adding 90% aqueous lactic acid. A margarine fat blend (500 parts) at 80° was added while the mixture was vigorously stirred, followed by a further amount (300 parts) at 80° with moderate stirring. The resulting 80% oil-in-water emulsion, which had a mayonnaise-like consistency, was cooled with moderate stirring to about 8° to effect partial crystallisation of the fat and then kneaded to give a phase-inverted margarine.

EXAMPLE 8

The partially hydrolysed defatted soya phosphatide fraction (8 parts by weight) of Example 7 was dispersed in a mixture at 70° of sour milk (100 parts), fresh skim milk (100 parts) and whey powder (3 parts) having a pH of 4.8. Phosphatide-free butter oil (500 parts) at 70° was added to the mixture with vigorous stirring, followed by a further amount (300 parts) at 70° with moderate stirring. The resulting homogeneous 80% oil-in-water emulsion had a mayonnaise-like consistency. It was cooled slowly without working to about 9° to effect partial crystallisation of the fat and then worked to give a product of butter-like plasticity and elasticity which remained on storage for several weeks. At refrigerator temperature (5°) the product was as easy to spread as normal butter at from 15 to 20°.

EXAMPLE 9

A crude rapeseed oil phosphatide defatted by acetone extraction (100 g) having a lecithin (phosphatidylcholine) content of 23.4% by weight and a cephalin (phosphatidylethanolamine) content of 16.2% (as determined by thin layer chromatography using the method of Wagner, *Fette, Seifen, Anstrichmittel*, 1961, *63*, 1119) was dispersed in twice its weight of tap water. To the mixture was added powdered pancreatin (2 g) which had been previously heated to 78° for 30 minutes, the mixture kept at 50° for 6 hours, and then dried by evaporation under reduced pressure at 50°C. Analysis showed that about 65% of the lecithin had been converted to lysolecithin and about 75% of the cephalin had been converted to lysocephalin. After removal of free fatty acid by acetone extraction, the product contained 12% of lysolecithin and 8% of lysocephalin by weight. The partially hydrolysed rapeseed oil phosphatide was then used to prepare an oil-in-water emulsion as described in Example 1.

EXAMPLE 10

Sunflower oil (300 g) at 70° was gradually added to an aqueous dispersion (100 g) at 70° containing a soluble soya protein fraction (2.5 g) and the partially hydrolysed defatted soya phosphatide fraction (1.5 g) of Example 7, with vigorous stirring: the finely-divided pourable 75% oil-in-water emulsion (containing 0.2% of monoacylglycerophosphatide by weight of fat) obtained was stable at temperatures from 0° and 70° and could be diluted with water.

WHAT WE CLAIM IS:—

1. An aqueous fat emulsion containing phosphatide at least 15% by weight of which is a monoacylglycerophosphatide whose acyl group is derived from a fatty acid having at least 8 carbon atoms.

2. An emulsion according to Claim 1, in which at least 25% of the phosphatide is the monoacylglycerophosphatide.

3. An emulsion according to Claim 1 or Claim 2, where the acyl group of the monoacylglycerophosphatide has at least 10 carbon atoms.

4. An emulsion according to any preceding claim, in which the monoacylglycerophosphatide is an α-monoacylglycerophosphatide.

5. An emulsion according to Claim 4, in which the monoacylglycerophosphatide comprises lysolecithin.

6. An emulsion according to Claim 5, in which the monoacylglycerophosphatide comprises lysolecithin and lysocephalin, the proportion of lysolecithin to lysocephalin being at least 4 to 1 by weight.

7. An emulsion according to any one of Claims 4 to 6, in which the monoacylglycerophosphatide is one that has been obtained by the action of phospholipase A on a diacylglycerophosphatide.

8. An emulsion according to Claim 7,

where the phospholipase A used was obtained by the partial heat-inactivation of pancreatin.

9. An emulsion according to Claim 7 or Claim 8, where the diacylglycerophosphatide used was a soyabean phosphatide.

10. An emulsion according to any preceding claim where the fat comprises vegetable fat.

11. An emulsion according to any one of Claims 1 to 9 where the fat comprises butter oil.

12. An emulsion according to any preceding claim, and containing from 3 to 85% fat by weight.

13. An emulsion according to Claim 12, and containing from 60 to 85% fat by weight.

14. An emulsion according to any preceding claim, and containing from 0.1 to 15% of the monoacylglycerophosphatide by weight of the fat.

15. An emulsion according to any preceding claim and containing water-soluble protein.

16. An emulsion according to any preceding claim and whose pH is from 4 to 5.

17. An emulsion according to any preceding claim, and comprising oil-in-water emulsion.

18. An emulsion according to any one of Claims 1 to 16, and comprising water-in-oil emulsion.

19. A fat emulsion substantially as described in any one of Examples 1 to 7.

20. A fat emulsion substantially as described in any one of Examples 8 to 10.

21. A process for preparing an emulsion according to any preceding claim, in which liquid fat is emulsified with an aqueous dispersion of the monoacylglycerophosphatide-containing phosphatide to produce an oil-in-water emulsion.

22. A process according to Claim 21, in which an oil-in-water emulsion of 35 to 85% fat content is prepared and is then cooled to at least 5°C below the melting point of the fat phase.

23. A process according to Claim 22, in which the cooled oil-in-water emulsion is worked to cause phase inversion and produce a water-in-oil emulsion.

24. A process for preparing a fat emulsion substantially as described in any one of Examples 1 to 7.

25. A process for preparing a fat emulsion substantially as described in any one of Examples 8 to 10.

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